

## Ph 3504

# Nuclear Magnetic Resonance and Electron Spin Resonance

### Required background reading

Tipler, Llewellyn, section 12-3 (you only need to read the part labeled “Nuclear Magnetic Resonance” on pages 596 - 597)

### Prelab Questions

1. For the “nuclear magnetic resonance” part of this experiment, you will be determining the NMR “resonance” frequency for protons in different molecules. The resonance frequency will be slightly different in different molecules because the internal magnetic field experienced by the proton (due to the surrounding electrons and nuclei) is slightly different. Assume that you observe a difference in the resonance frequency of 0.1 MHz between two different molecular samples. What difference in internal magnetic fields does this correspond to?
2. For the electron spin resonance (ESR) part of the experiment everything will be the same as for the proton EXCEPT the magnetic moment of the electron is much larger than that of the proton. In fact the magnetic moment of the electron is 1 Bohr magneton, where the Bohr magneton is defined on page 309 of your textbook. Evaluate what magnetic field is needed to get an ESR resonance of 10 MHz for an electron. (You basically use the same formula as on page 597 for the proton except you replace the magnetic moment of the proton with the magnetic moment of the electron).

### Introduction

Elementary particles have magnetic moments. In this lab, we will make measurements that involve the magnetism of the electron (electron spin resonance) and the proton (nuclear magnetic resonance). The NMR technique is commonly used in medicine to make non-invasive three dimensional images of internal tissues and organs; it is referred to in medicine as MRI (magnetic resonance imaging).

When a magnetic moment is placed in a magnetic field the potential energy is:

$$U = -\vec{\mu} \cdot \vec{B}$$

where  $\mu$  is the magnetic moment of the particle. For a spin  $\frac{1}{2}$  particle there are two quantum states that correspond to two different energies – magnetic moment parallel to

the magnetic field and magnetic moment anti-parallel to the magnetic field. The energy splitting between these two states is given by:

$$\Delta E = 2\mu B$$

where  $B$  is the strength of the magnetic field that we place the particle in. We can cause transitions between these two energy levels by applying an oscillating electromagnetic field at the frequency  $f$  corresponding to the energy difference in the above expression:

$$f = \frac{\Delta E}{h} = \frac{2\mu B}{h}$$

We refer to this frequency as the **resonance** frequency. The magnetic moment for the electron and proton respectively are:

$$\text{electron : } \mu_e = \mu_B = \frac{e\hbar}{2m_e} = 5.79 \times 10^{-5} \text{ eV/T}$$

$$\text{proton : } \mu_p = 2.79\mu_N = (2.79)\frac{e\hbar}{2m_p} = (2.79) 3.15 \times 10^{-8} \text{ eV/T}$$

where  $\mu_B$  and  $\mu_N$  are referred to as the Bohr magneton and nuclear magneton, respectively. Using the value of Planck's constant ( $h = 4.14 \times 10^{-15} \text{ eV}\cdot\text{s}$ ), we have the following relations between the resonance frequency (in MHz) and applied magnetic field (in Tesla):

$$\text{electron : } f(\text{MHz}) = (28.0 \times 10^3) \text{ B(T)}$$

$$\text{proton : } f(\text{MHz}) = (42.5) \text{ B(T)}$$

When the frequency  $f$  of the applied oscillating magnetic field is equal to the resonant frequency, energy is absorbed from the electrical circuit that is attached to it. This is because the magnetic moments transition from the lower energy level (magnetic moment and B field parallel) to the upper energy level (magnetic moment and B field anti-parallel). In the process they absorb one quanta (photon) of energy from the oscillating electromagnetic field.

Experimentally, there are two ways to find the resonance for a given sample. One can run with a fixed magnetic field  $B$  and vary the frequency  $f$  of the oscillating electromagnetic field until resonance is observed. Alternatively, one can run with a fixed frequency  $f$  of the oscillating electromagnetic field, and vary the applied magnetic field  $B$  until resonance is observed. We will do the latter in this experiment.

## Procedure

In this lab you will use the digital oscilloscope to study the waveforms. In the first part of this lab, you will go through some steps to familiarize yourself with the operation of the oscilloscope. You will be using the Tektronix TDS 1002 oscilloscope; it is a two channel digital oscilloscope. One of the very nice features of the Tektronix TDS 1002 oscilloscope is its ability to be connected to a computer. This allows the computer to both control the oscilloscope and record data from it. You will use this feature to print the display of the oscilloscope.

Turn on the oscilloscope and go through the introduction to the most important controls below. Take time to locate each **bold-faced** item when it is mentioned.

Many of the functions of the Tektronix TDS 1002 oscilloscope are controlled by the use of menus. When a menu button is pressed the menu options for that button are displayed on the right side of the oscilloscope screen. Five selection buttons along the right side of the screen are used to select from the various menu options that are available. When the selection button next to menu item is pressed the option will toggle through several setting choices for that option. If the button pressed enough time it will return to the original setting. There are three menu buttons that are of general use on the oscilloscope they are the **CH1**, **CH2**, **TRIG** menu buttons. In this part of the lab you will be exploring some of the functions in these menus as well as some of the other controls of the oscilloscope.

### CH1 and CH2 Menu Buttons

The oscilloscope has two channels (**CH1** and **CH2**) that can measure voltages independently. The settings for each of these channels are menu driven. By pressing the **CH1** or **CH2** menu button various options can be selected. Pressing the menu button once turns on the channel. Pressing the menu button a second time turns off the channel. When the channel is selected **CH1** or **CH2** appears above the menu indicating that the menu options will be applied to that channel. If two channels are turned on at the same time then one of the channels will be selected and its label (**CH1** and **CH2**) will appear above the menu option on the screen. To select the other channel simply press its menu button.

The options that are most important on the **CH1** and **CH2** menus are the ‘coupling’ and the ‘probe’ settings. The ‘coupling’ option has three settings, DC, AC, and Ground. In the DC setting you see the total signal voltage. In the AC position the DC (direct current) portion of the signal is “blocked” (i.e., the mean value of the signal is subtracted), which is useful if you want to investigate a small, time-varying signal sitting on a large DC voltage. In the Ground setting the input is grounded, so that you have a zero reference point. The probe setting should be set to “x1”. **By default it comes up as “x10”; please set it to “x1”.**

## Channel Controls for Channels 1 and 2 (CH1 and CH2)

Each channel (**CH1** and **CH2**) has the following set of independent controls:

- A gain setting that sets the number of **VOLT/DIVISION**. This value is displayed on the bottom of the oscilloscope screen.
- A vertical position control, above the **CH1** and **CH2** menu buttons.

### Trigger (TRIG) Menu button

The oscilloscope sweeps out a trace of the voltage as a function of time. The oscilloscope needs to know when to start this sweep. The trigger signal is the way the oscilloscope determines when to start the sweep. The **TRIG** menu button allows you to tell the oscilloscope what signal to trigger the sweep on and on what part of that signal. The options on the TRIGGER menu that are most often used are Type, Source, Slope, and Mode. The trigger Type option will always be set to 'Edge' in this lab but in other setting is useful when looking at special signal such as those from a video source. The trigger Source option is the voltage signal that will start the sweep. This signal can come from either **CH1** or **CH2**, an external line, or from the 60 Hz AC power sources. Usually the trigger signal will come from **CH1** or **CH2**. The Slope option allows the sweep to be triggered either when the trigger signal is rising or falling. In this lab triggering on the rising signal will work for all the cases we will do. The Mode option has two settings: Auto and Normal. In the Auto setting the trigger is automatic so that the sweep display is visible even if there is no input signal. This is most useful for setting up and for looking at DC voltages. When the Mode option is set to Normal the sweep starts only when the trigger source changes as was selected in the other setting.

### Trigger Controls

The level of the signal that triggers the sweep can be adjusted by using the trigger Level knob. A small arrow appears on the right side screen indicating the level of the trigger voltage on the trigger sources (**CH1** and **CH2**). The **SET TO 50%** sets the trigger level automatically to 50% of the current trigger source. This is a very convenient feature to find an appropriate trigger level. The **FORCE TRIG** button forces the oscilloscope to trigger in Normal mode even if it doesn't see a trigger signal on the source. The **TRIG VIEW** button allows the trigger setting to be displayed on the bottom of the screen.

Before moving on, set the scope settings as follows:

- Select channel 1 by pressing the **CH1** menu button
- Press the "Coupling" menu until AC is displayed
- Press the "Probe" menu until "x1" is displayed
- Select channel 2 by pressing the **CH2** menu button
- Press the "Coupling" menu until AC is displayed
- Press the "Probe" menu until "x1" is displayed
- Press the **TRIG MENU** button and select **AUTO** trigger mode
- Press the "**SET TO 50%**" TRIGGER LEVEL button

- Set the horizontal sweep rate (sec/div) to 250  $\mu$ sec/div, the value is displayed on the bottom of the screen next to an “M”

You should see two flat scope traces; if you don’t adjust the position knobs for each channel. Adjust CH1 so that it is at two major divisions above the center of the screen grid. Place the CH2 trace at two major divisions below the center of the grid. It is a good practice to keep the CH1 trace on the upper half of the display and the CH2 trace on the lower half.

## Function Generator

In its basic application, a function generator produces a repeating voltage pattern, where you may select one of several forms, the amplitude, and the frequency. You will be using the BK Precision 4017A Function Generator. Turn it on and set the following settings on the front panel:

### FREQUENCY

<b>Range selection</b>	Depress 1K button
<b>Coarse/fine controls</b>	Adjust for digital readout of 1000 Hz (note that there is a delay in the response)
<b>Function</b> (not labeled with words only symbols)	Depress the button for sine wave.
<b>Duty Cycle</b>	off (button out), ignore the knob settings
<b>CMOS LEVEL</b>	off (button out), ignore the knob settings
<b>DC OFFSET</b>	off (button out), ignore the knob settings
<b>-20 dB</b>	off (button out), ignore the knob settings
<b>OUTPUT LEVEL</b>	Rotated knob to the center position

Use a cable (with BNC connectors on both ends) to connect the output of the function generator to CH1 of the scope. You should now see a signal on one trace and no signal on the other. Initially the signal will probably not be triggered properly, so it will appear “free-running” or random. Set the trigger **MODE to NORM** and to trigger on CH1. When you are in this configuration, a horizontal sweep will be initiated whenever the signal in CH1 passes a certain voltage level. To set this level, turn the LEVEL knob until you achieve a stable trace. As you turn the LEVEL knob, notice how it affects the point where the trace starts (the trigger level). Also, try changing the SLOPE that you trigger on from Rising to Falling on the TRIG MENU. When the scope is triggered properly, it will say “Trig’d” at the top; when it is not triggered it says “Ready”.

Select Channel 1 and change the “Coupling” to DC. Adjust the gain and vertical position so that the sine wave amplitude fits in the screen and is centered vertically.

Also try the cursor button to set a cursor to measure time differences; ask your TA for help on how this works.

Here is the procedure for capturing oscilloscope waveforms on the computer:

1. Under programs, open the OpenChoice Desktop software.
2. Click on “Select Instrument”
3. Highlight “ASRL1::INSTR”
4. Click on “OK”
5. Click on “Screen Capture”
6. Click on “Get Screen”. This operation takes 1-2 minutes; if it fails just try clicking “Get Screen” again.
7. Click on “Copy to Clipboard.”
8. Start a Word document where you can paste all of your images from this lab. Go ahead and paste the image of whatever is on the scope at the moment.

Now we will begin making measurements:

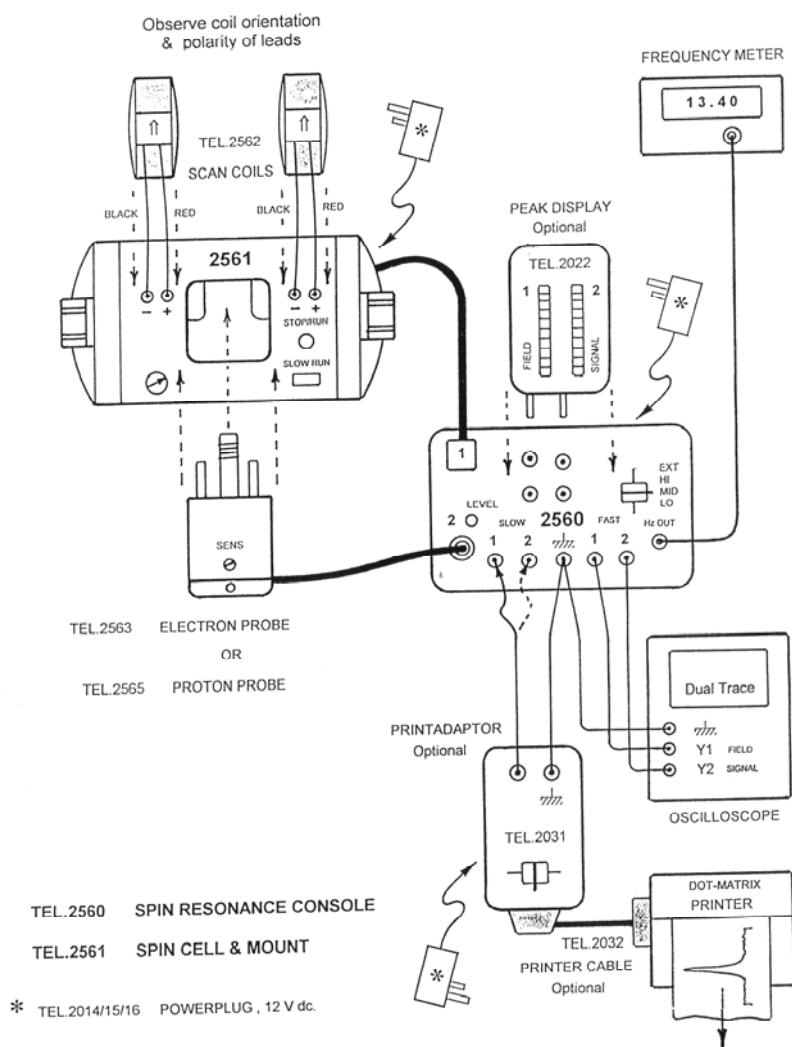


Figure 1: Apparatus setup. We are not using the “Peak Display” or “Print/Adapter”. The Frequency Meter is the digital multimeter set in “Hz” mode.

## ESR (Electron Spin Resonance)

1. First look at the setup. The coils provide the fixed magnetic field  $B$ . The attached circuitry sweeps the value of the  $B$  field using a linear ramp function. The value of the  $B$  field is swept from 0 to  $3.67 \times 10^{-3}$  T over a period of 40 msec. This linear ramp is continued over and over and you will capture it on the oscilloscope. Plug the output of “Fast 1” on the NMR/ESR control console to channel 1 of the oscilloscope. This will display the linear ramp function. Set your oscilloscope settings as follows to get a good display:

**TRIGGER menu:** Trig: edge  
Source: CH 1  
Slope: rising  
Mode: Norm  
Coupling: DC

**CH1 menu:** Coupling: Dc  
BW/limit: OFF  
Volts/div: coarse  
Probe: 1x  
Invert:OFF

Set the CH1 vertical gain to 200 mV/division and the horizontal timebase to 5 msec/div. You should see a single cycle of the linear ramp function (you may need to adjust the trigger level, since you are in NORMAL mode). Adjust it vertically to the top part of your screen. Horizontally, adjust it so that the beginning of the ramp occurs at one of the vertical lines on the screen. You will need to judge timing relative to this point, so it is convenient to have it aligned with a vertical line. Once you have made this horizontal adjustment, don't change it again for the rest of this ESR part. Set up the horizontal cursor to allow you to measure times relative to the start of the linear ramp function. Your TA can show you how to do this.

2. Now look at the thing labeled “electron probe”. If there is a source (a small vial) inserted on the backside, remove it and put it in the Styrofoam tray. Then remove the electron probe to look at it. You should notice the tightly wound coils at the end of the tip. That is where the oscillating current is passed through to provide the oscillating magnetic field at frequency  $f$ . Reinstall the electron probe with the label saying “SENS” pointing upward. You should see a little screw in there. It is used to control the level of oscillations in the probe electronic circuit; increasing the sensitivity from the minimum reduces the oscillator level. For now, use the screwdriver provided to set the SENS to maximum, which is completely counter-clockwise. You should see the red LED indicator on CH2 of the ESR/NMR console lit.

3. Plug the output from “Fast2” output on the ESR/NMR console into CH2 of the oscilloscope. Adjust the CH2 settings as follows:

**CH2 menu:**           Coupling: Dc  
                           BW/limit: OFF  
                           Volts/div: coarse  
                           Probe: 1x  
                           Invert:OFF

and set its gain to 200 mV/div. You should see a display like that shown in the left half of Figure 2; if you are having problems, consult with your TA.

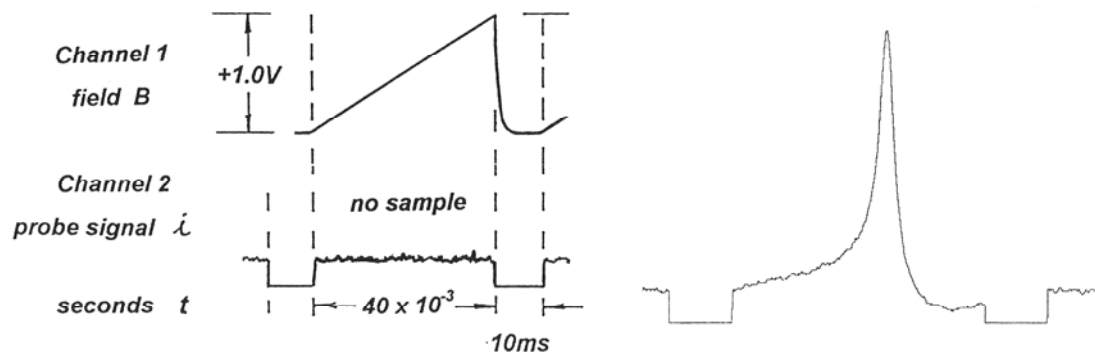


Figure 2: Expected output on the oscilloscope for the ESR experiment. The left half shows the CH2 output with no ESR signal, and the right half shows a typical resonance signal from a real sample.

4. Adjust the slider button on the NMR/ESR control panel to the “MID” setting. Check that the frequency meter is attached; it should read about 60 kHz (**NOTE:** The actual applied frequency is 1000 times the frequency read out on the meter; so if the meter reads 60 kHz then the actual applied frequency is 60 MHz). Locate the **orange** colored sample vial. This contains a small sample of a complex molecule diphenyl-picri-hydrazyl, DPPH. For our purposes, the important point is that this paramagnetic compound has a loosely bound unpaired electron which is the electron that we will be determining the ESR resonance for.

5. Initially, you should see a flat line in Channel 2 as shown in the left half of Figure 2. To observe the resonance you need to adjust the sensitivity by turning the SENS knob clockwise. As you turn the knob clockwise, you should start to see a resonance peak appear. You will also notice that the **signal level indicator** LED of Channel 2 will begin to get fainter as you get a good signal. If you turn too far clockwise that LED will turn OFF, indicating oscillations have stopped. That means you have gone too far and you have to turn back to get into the sensitive range again.

6. Once you have a good clear resonance, use the cursor to determine at what time shift (relative to the start of the ramp) that the center of the peak occurs. You will need this information later to determine what the applied magnetic field  $B$  was on the resonance. Print your oscilloscope screen to your Word document. **Be sure to label the document to indicate what the frequency read on the DMM is. Make sure your cursors are set to measure the time difference so that number will be recorded in your printout.**

7. According to the discussion in the introduction, the resonance frequency is linearly proportional to the applied magnetic field. You will now demonstrate that by trying two different frequencies and determining what magnetic field is needed to achieve resonance.

8. Switch the frequency slider switch to “HI”. With the SENS knob turned fully counter-clockwise, you should see a frequency of around 77 kHz. Now adjust the SENS knob to get a good resonance trace like you did in step 6. Repeat everything you did in step 6 for this frequency.

9. Now try a low frequency by putting the slider switch to “LO”. With the SENS knob turned fully counter-clockwise, you should see a frequency of around 44 kHz. Now adjust the SENS knob to get a good resonance trace like you did in step 6. Repeat everything you did in step 6 for this frequency.

10. You should have 3 printouts in your Word document – a printout for each of the three frequencies you looked at. Each should be labeled with the frequency, and the time of the ESR peak relative to the start of the ramp should be clearly indicated. You are done with this part; move on to the NMR part when the setup is free.

## **NMR (Nuclear Magnetic Resonance)**

1. First look at the setup. This unit is equipped with an electromagnet. It has an iron core that provides a strong field. We need a stronger field than we used in the ESR experiment because the magnetic moment of the proton is ~1800 times smaller than that of the electron due to its larger mass. To vary the applied magnetic field we vary the current in the “trim coils” surrounding the iron core. The attached circuitry sweeps the value of the B field using a linear ramp function. The value of the B field is swept from over about 1% of its range in 0 to 40 msec. For your magnet, that corresponds to going from a field of 0.3188 T to 0.3220 T in 40 msec. This linear ramp is continued over and over and you will capture it on the oscilloscope. Plug the output of “Fast 1” on the NMR/ESR control console to channel 1 of the oscilloscope. This will display the linear ramp function. Set your oscilloscope settings as follows to get a good display:

**TRIGGER menu:** Trig: edge  
Source: CH 1  
Slope: rising  
Mode: Norm  
Coupling: DC

**CH1 menu:** Coupling: Dc  
BW/limit: OFF  
Volts/div: coarse  
Probe: 1x

Invert:OFF

Set the CH1 vertical gain to 200 mV/division and the horizontal timebase to 5 msec/div. You should see a single cycle of the linear ramp function. Adjust it vertically to the top part of your screen. Horizontally, adjust it so that the beginning of the ramp occurs at one of the vertical lines on the screen. You will need to judge timing relative to this point, so it is convenient to have it aligned with a vertical line. Once you have made this horizontal adjustment, don't change it again for the rest of this NMR part. Set up the horizontal cursor to allow you to measure times relative to the start of the linear ramp function. Your TA can show you how to do this. Finally, use the oscilloscope program on the computer to print out a copy of channel 1 on the printer; print a copy for each partner.

2. Now look at the thing labeled "proton probe". If there is a source (a small vial) inserted on the backside, remove it and put it in the Styrofoam tray. Then remove the proton probe to look at it. You should notice the tightly wound coils at the end of the tip. That is where the oscillating current is passed through to provide the oscillating magnetic field at frequency  $f$ . Reinstall the electron probe with the label saying "SENS" pointing upward. You should see a little screw in there. It is used to control the level of oscillations in the probe electronic circuit; increasing the sensitivity from the minimum reduces the oscillator level. For now, use the screwdriver provided to set the SENS to maximum, which is completely counter-clockwise. You should see the red LED indicator on CH2 of the ESR/NMR console lit.

3. Plug the output from "Fast2" output on the ESR/NMR console into CH2 of the oscilloscope. Adjust the CH2 settings as follows:

**CH2 menu:**           Coupling: Dc  
                          BW/limit: OFF  
                          Volts/div: coarse  
                          Probe: 1x  
                          Invert:OFF

and set its gain to 200 mV/div. You should see a display like that shown in the left half of Figure 2; if you are having problems, consult with your TA.

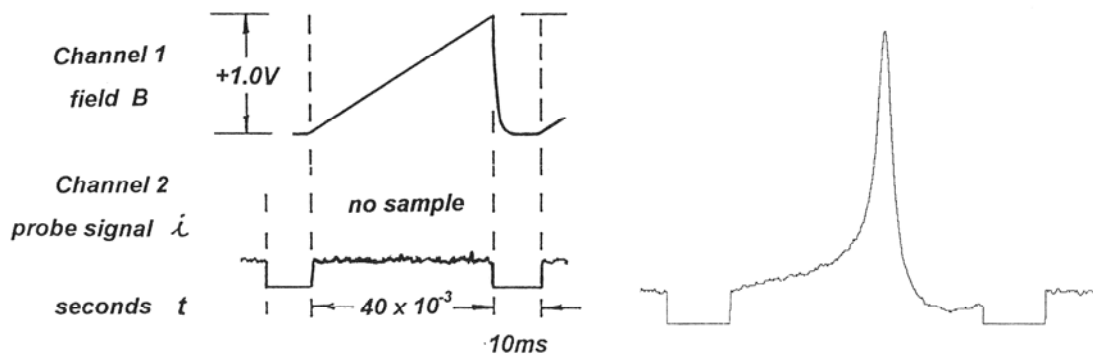


Figure 3: Expected output on the oscilloscope for the NMR experiment. The left half shows the CH2 output with no NMR signal, and the right half shows a typical resonance signal from a real sample.

4. Adjust the slider button on the NMR/ESR control panel to the “HI” setting. Check that the frequency meter is attached. Locate the **yellow** colored sample vial. This contains a small sample of glycerine. We will be looking at NMR resonances transitions for protons in the nuclei of its atoms.

5. Initially, you should see a flat line in Channel 2 as shown in the left half of Figure 2. To observe the resonance you need to adjust the sensitivity by turning the SENS knob clockwise. As you turn the knob clockwise, you should start to see a resonance peak appear. You will also notice that the **signal level indicator** LED of Channel 2 will begin to get fainter as you get a good signal. If you turn to far clockwise that LED will turn OFF, indicating oscillations have stopped. That means you have gone too far and you have to turn back to get into the sensitive range again. If you do not see a resonance, then leave the SENS screw set on a sensitive setting. You will now need to do the steps in the next section to adjust the frequency to be in the right range.

6. Remove the glycerine sample. Withdraw the proton probe unit from the cell column and reinsert it upside down with the FREQ knob pointing upwards. Replace the glycerine sample vial and adjust the FREQ knob until a resonance peak is observed. The resonance frequency should be somewhere in the range 13 – 14 kHz (**Note:** the actual applied frequency is 1000 times this ~ 13 – 14 MHz). The peak should look similar to the peak in Figure 4.

7. Once you have a good clear resonance, use the cursor to determine at what time shift (relative to the start of the ramp) that the center of the peak occurs. You will need this information later to determine what the applied magnetic field  $B$  was on the resonance. Use the computer program to print out your Channel 2 trace; one for each partner. **Be sure to label your plot with the observed time shift from your cursor measurement AND the frequency from the frequency meter AND the name of the sample (glycerine).**

8. In addition to the externally applied magnetic field, the protons in nuclei also experience internal magnetic fields from nearby protons, neutrons, and electrons. These internal fields differ according to the type of molecule. So now you will determine the NMR resonance in two other molecular samples to see this effect.

9. Remove the glycerine sample and insert the polystyrene sample (**green** vial). Repeat steps 5 – 7 for this sample.

10. Remove the polystyrene sample and insert the Polytetrafluorethylene (PTFE) sample (**blue** vial). You will need too set the frequency slider switch to “MID” for this sample. Repeat steps 5 -7 for this sample. This frequency will be in the range 12 – 13 kHz (12 – 13 MHz actual frequency).

11. You should have 4 printouts – the linear ramp, and a printout for each of the three samples you looked at. You are done with this part; move on to the ESR part (unless you did that part first).

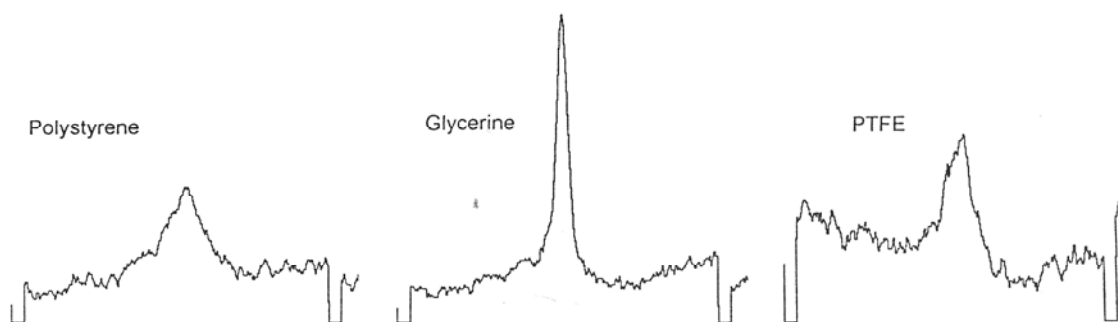


Figure 4: Expected resonance peaks for the three NMR samples.

## Report

The reading on page 596 – 597 in Tipler will be helpful in preparing your lab report.

Make sure your report for this lab includes all of the following:

1. Introduction

2. Analysis of ESR data:

- Show explicitly (with a formula) how you determine the magnetic field  $B$  for each of the three data points you took. Make an estimate of your error on the magnetic field determination (limited mainly by your ability to determine the exact position of the ESR peak).

- You should have three pairs of points ( $B, f$ ) where  $f$  was the oscillating magnetic field frequency and  $B$  was the applied magnetic field where you observed the ESR resonance. Make a plot of  $f$  vs.  $B$  to see if the functional form is in agreement with what you expect (see the introduction to the lab if you aren't sure what to expect). (Remember that the frequency read on the meter needs to be multiplied by a factor of 1000 to get the actual frequency).
- Do a least squares fit to your data to get the best estimate of the slope. From the slope, quote what your measured value for the Bohr magneton (magnetic moment of the electron) is. Compare your result to the accepted value of the Bohr magneton.

### 3. Analysis of NMR data:

- From your data, determine the magnetic field  $B$  and frequency  $f$  at which resonance occurred for each of your three samples (glycerine, polystyrene, and PTFE). Make an estimate of the error of your magnetic field determination as you did for the ESR data.
- In glycerine and polystyrene, the protons are primarily in hydrogen atoms. For the purposes of this analysis, you can assume that these are “free” protons, and you can directly extract the magnetic moment of the proton from them. Determine the value of the magnetic moment of the proton (and its error) from each of these two samples. Combine them to get your best measurement of the proton's magnetic moment (and its error). Compare to the accepted value.
- The protons in the PTFE sample are mostly in fluorine nuclei. They experience a different internal magnetic field (compared to glycerine and polystyrene) due to the presence of the other protons in the fluorine nucleus. From the shift in the observed resonance frequency of PTFE (relative to glycerine and polystyrene) extract the value of the internal magnetic field at the proton in PTFE. (Note: Here “external” magnetic field is the field applied by the external magnet, whereas internal magnetic field is the local field at the protons in the fluorine nucleus due to the presence of the other protons.)

4. Explain in a few sentences how the technique of NMR is used in medical imaging (where it is called MRI – magnetic resonance imaging).

### 5. Conclusion